

# PATENT ABSTRACTS OF JAPAN

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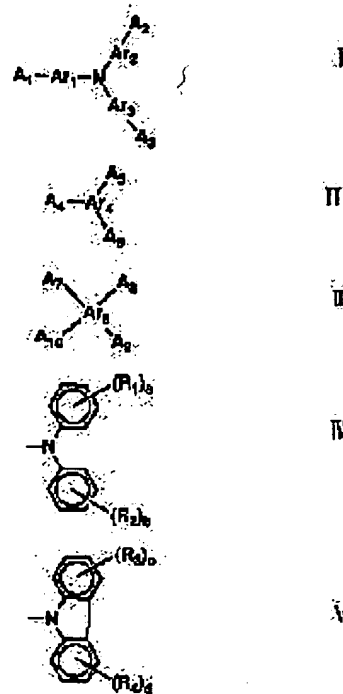
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## (54) ORGANIC ELECTROLUMINESCENT ELEMENT

(57)Abstract:

PURPOSE: To obtain the subject element having improved thermal stability and excellent luminescent characteristics and suitable as a surface light source, etc., for back light by using a specific compound as a hole-transporting material constituting a luminescent layer or a hole-transporting layer.

CONSTITUTION: The objective element is produced by preparing a luminescent layer containing a hole-transporting material consisting of an aromatic amine compound of formula I to formula III [Ar1 to Ar5 are  $\geq 6$ C aromatic hydrocarbon group or  $\geq 4$ C aromatic heterocyclic group containing hetero atoms; A1 to A10 are group of formula IV, formula V (R1 to R4 are H, 1-12C alkyl, etc.; (a) and (b) are 0-5; (c) and (d) are 0-4), etc.] or a luminescent layer containing a luminescent compound and a hole-transporting layer containing the above hole-transporting material and sandwiching the layers between a pair of



electrodes at least one of which is (semi)transparent. The hole-transporting material is e.g. 4,4',4''-tris(diphenylamino) triphenylamine and the luminescent material is e.g. tris(8-quinolinol)aluminum.

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## LEGAL STATUS

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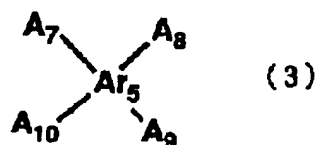
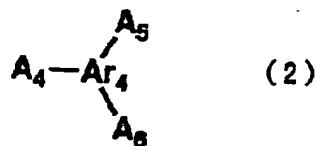
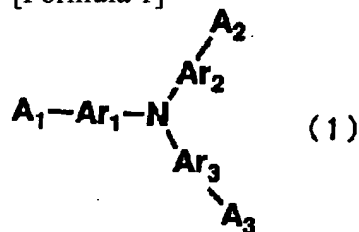
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## CLAIMS

[Claim(s)]

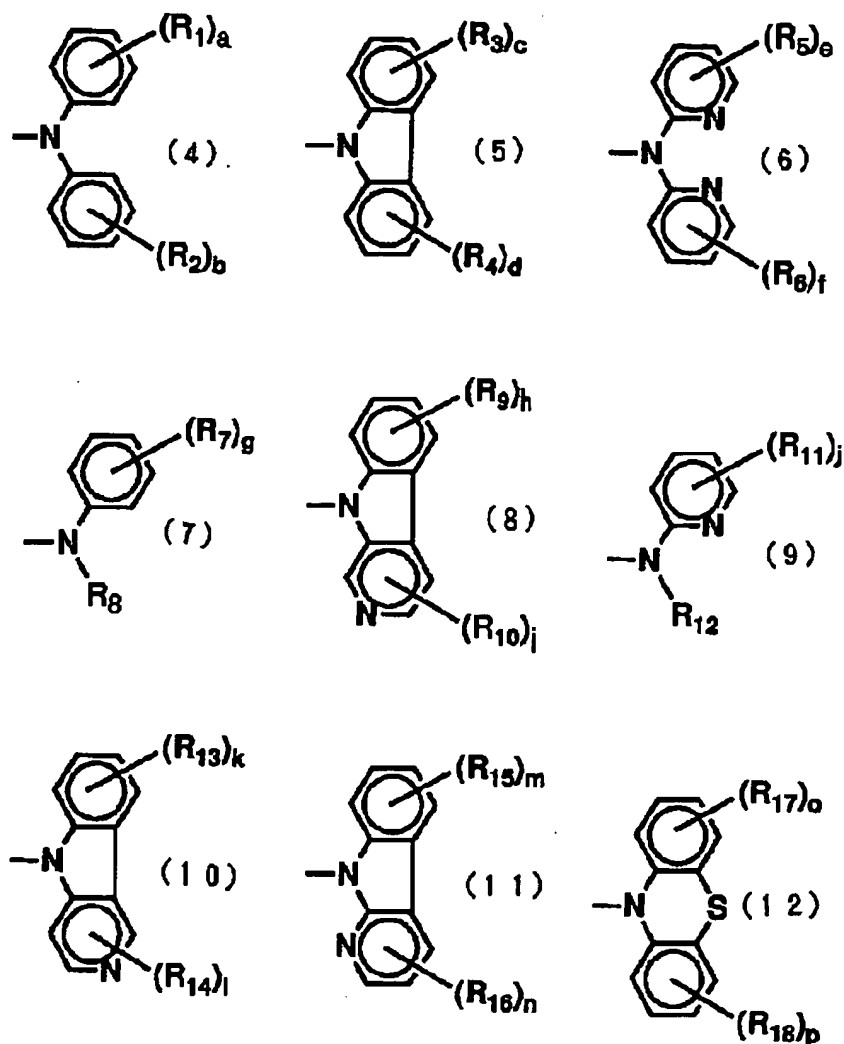
[Claim 1] At least one side is the electroluminescent element which has an electron hole transportation layer containing the luminous layer which contains luminescent material and an electron hole transportation ingredient in inter-electrode [ of transparence or a translucent pair ] at least or the luminous layer which contains luminescent material at least, and an electron hole transportation ingredient, and it is following general formula (1) - (3) as this electron hole transportation ingredient.

[Formula 1]



The inside Ar1 of [type, Ar2, Ar3, Ar4, and Ar5 express the aromaticity heterocyclic compound radical which contains a with a carbon numbers of six or more aromatic hydrocarbon radical or a with a carbon numbers of four or more hetero atom independently, respectively. A1, A2, A3, A4, A5, A6, A7, A8, A9, and A10 show independently the radical chosen from following general formula (4) - (12), respectively.

[Formula 2]



(R1 -R7, R9 -R11, and R13-R18 are the radicals independently chosen from hydrogen, the alkyl group of carbon numbers 1-12 and an alkoxy group, the aryl group of carbon numbers 6-14 and the aryloxy group, the nitro group, and the aromaticity heterocyclic compound radical, respectively, and when two or more substituents are in the one benzene ring or a pyridine ring, even if they are the same, they may differ.) R8, the radical as which R12 were independently chosen from hydrogen and the alkyl group of carbon numbers 1-12, respectively, a, b, c, d, e, f, g, h, i, j, k, l, m, n, o, and p, respectively Zero  $\leq a, b, g \leq 5$ ,  $0 \leq c, d, e, f, h, j, k, m$  and  $o, p \leq 4$ , and  $0 \leq n \leq 3$ . the organic electroluminescent element characterized by containing at least a kind of aromatic amine compound chosen from the compound expressed with i, l, and integer] of  $n \leq 3$ .

[Claim 2] The organic electroluminescent element according to claim 1 which an electron hole transportation layer becomes from the thing which made the high molecular compound distribute an aromatic amine compound according to claim 1.

[Claim 3] The organic electroluminescent element according to claim 1 which consists of a thing to which the luminous layer made the high molecular compound distribute an aromatic amine compound according to claim 1 and luminescent material.

[Translation done.]

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to an organic electroluminescent element (following organic EL device). It is related with the organic EL device which used the detailed specific aromatic amine compound for the charge transportation ingredient.

[0002]

[Description of the Prior Art] Although the inorganic electroluminescent element was used for displays, such as a source of sheet-like light as the former, for example, a back light, and a flat-panel display, etc., it needed the alternating current of the high voltage for making light emit. Recently, Tang and others produced the organic electroluminescent element which has the two-layer structure which made the organic fluorochrome the luminous layer and carried out the laminating of the electron hole transportation layer which becomes it from a triphenyl diamine derivative, and realized a low-battery direct-current drive, efficient, and the organic EL device of high brightness (JP,59-194393,A). Compared with an inorganic EL element, an organic EL device from there being a low-battery drive, high brightness, and the features that in addition luminescence of many colors is obtained easily Many attempts are reported about component structure, the organic fluorochrome, and the organic charge transportation compound (27 Japanese journal OBU applied physics (Jpn.J.Appl.Phys.)). L269(1988)] [the 65th volume (J. Appl.Phys.) of journal OBU applied physics and 3610 pages (1989)],

[0003]

[Problem(s) to be Solved by the Invention] Although the organic EL device reported so far is high brightness, there is a problem that the life of a light emitting device is short. As the reason, a structural change of an organic layer arises by generation of heat of a component, and it is said that it may deteriorate. Therefore, the charge transportation ingredient which constitutes a stable organic layer thermally was called for.

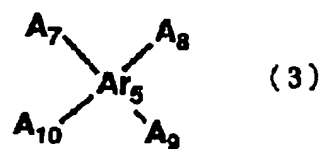
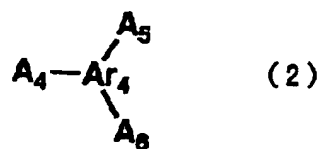
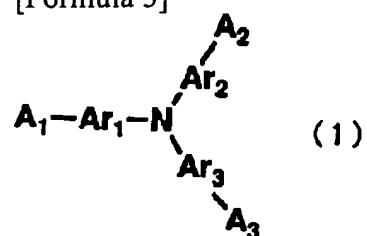
[0004] As a result of considering wholeheartedly the heat-resistant improvement in an organic EL device, by having a specific aromatic amine compound, for example, an aromatic series ring, or thoria reel amine structure in a frame as an electron hole transportability compound, and using the aromatic amine compound in which three or more place nuclear substitution was carried out by the amino group, this invention person etc. formed the uniform organic film, found out that the thermal stability of an organic EL device and the homogeneity of luminescence were improved, and resulted in this invention.

[0005]

[Means for Solving the Problem] That is, it sets to the electroluminescent element which has an electron hole transportation layer containing the luminous layer to which at least one side contains luminescent material and an electron hole transportation ingredient in inter-electrode [ of transparence or a translucent pair ] at least or the luminous layer which contains luminescent material at least, and an electron hole transportation ingredient, and this invention is following general formula (1) - (3) as this electron hole transportation ingredient.

[0006]

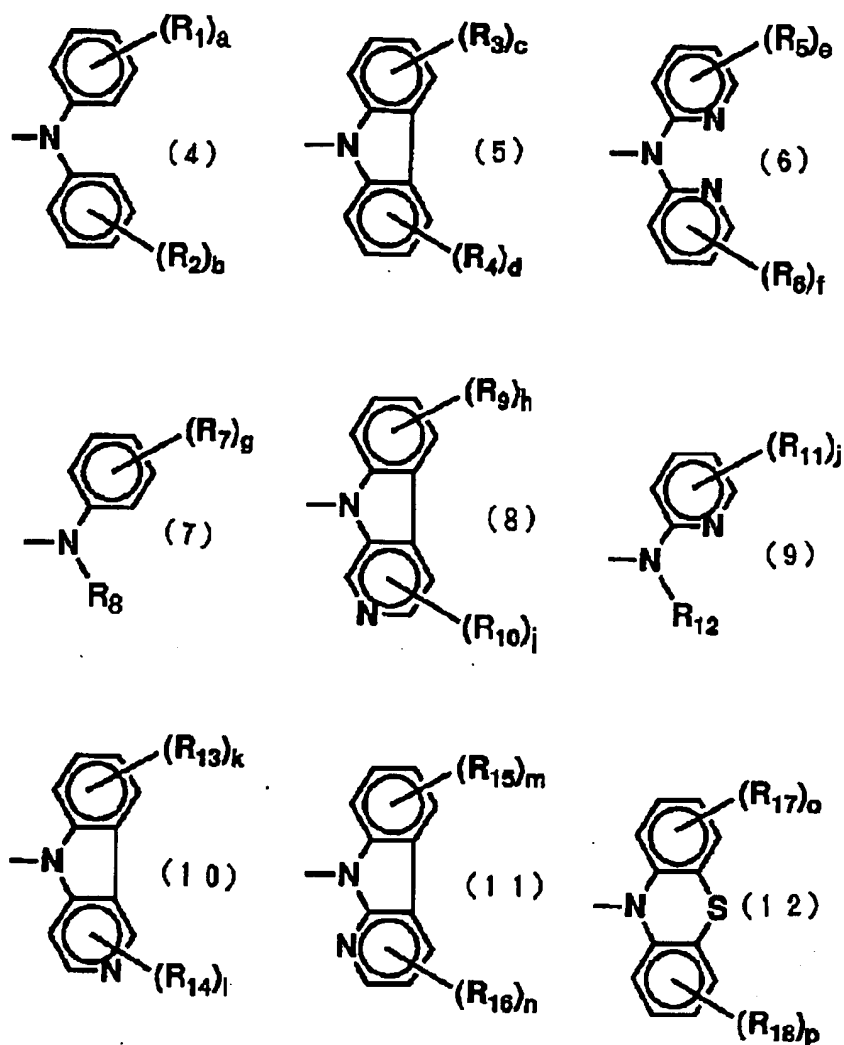
[Formula 3]



[0007] The inside Ar1 of [type, Ar2, Ar3, Ar4, and Ar5 express the aromaticity heterocyclic compound radical which contains a with a carbon numbers of six or more aromatic hydrocarbon radical or a with a carbon numbers of four or more hetero atom independently, respectively. n shows two or more integers, A1, A2, A3, A4, A5, A6, A7, A8, A9, and the radical as which A10 was chosen from following type (4) - (12) respectively and independently.

[0008]

[Formula 4]



[0009] (R1 -R7, R9 -R11, and R13-R18 are the radicals independently chosen from hydrogen, the alkyl group of carbon numbers 1-12 and an alkoxy group, the aryl group of carbon numbers 6-14 and the aryloxy group, the nitro group, and the aromaticity heterocyclic compound radical, respectively, and when two or more substituents are in the one benzene ring or a pyridine ring, even if they are the same, they may differ.) R8, the radical as which R12 were independently chosen from hydrogen and the alkyl group of carbon numbers 1-12, respectively, a, b, c, d, e, f, g, h, i, j, k, l, m, n, o, and p, respectively  $0 \leq a, b, g \leq 5$ ,  $0 \leq c, d, e, f, h, j, k, m$  and  $o, p \leq 4$ , and  $0 \leq n \leq 3$  -- it is in offering the organic electroluminescent element characterized by containing at least a kind of aromatic amine compound chosen from the compound expressed with i, l, and integer] of  $n \leq 3$ .

[0010] Hereafter, the organic EL device of this invention is explained to a detail. In this invention, the well-known thing which is not limited especially as a luminescent material of an organic EL device, for example, is indicated by JP,57-51781,A or 59-194393 official reports, such as coloring matter, such as a naphthalene derivative, an anthracene derivative, a perylene derivative, a poly methine system, a xanthene system, a coumarin system, and a cyanine system, 8-hydroxyquinoline and a metal complex of the derivative, aromatic amine, a tetra-phenyl cyclopentadiene derivative, and a tetra-phenyl butadiene derivative, etc. is usable.

[0011] Furthermore, conjugated-system macromolecule fluorescent substances, such as short Pori (p-phenylenevinylene) of the conjugation chain length of a publication and Pori (2, 5-diheptyl oxy--p-phenylenevinylene), etc. can be used for JP,3-244630,A.

[0012] These luminescent material can form a luminous layer more for adopting suitably the applying methods, such as a well-known approach, for example, vacuum evaporation technique, or a spin coating

method of the solution melted into a solvent, the casting method, a dipping method, the bar coat method, and the roll coat method, etc. according to a compound. When luminescent material is not a high molecular compound, it is desirable to use a vacuum deposition method in that delicate control of thickness is performed.

[0013] The electron hole transportation ingredient used for this invention is chosen from the aromatic amine compound expressed with the aforementioned general formula (1), (2), and (3). It sets to the aromatic amine compound expressed with a general formula (1), and they are Ar1, Ar2, and Ar3. It is the radical chosen independently of the aromaticity heterocyclic compound radical which contains a with a carbon numbers of six or more aromatic hydrocarbon radical or a with a carbon numbers of four or more hetero atom independently, respectively. Ar1, Ar2, and Ar3 \*\*\*\* -- although it is possible for it to be also a different radical, it is desirable that two or more radicals are the same, and all are more preferably the more nearly same than a composite ease.

[0014] Ar1, Ar2, and Ar3 If it carries out, as with a carbon numbers of six or more aromatic hydrocarbon Benzene, What was permuted by frames, such as a biphenyl, naphthalene, and an anthracene, two places is illustrated. 1, 4-phenylene, 1, 3-phenylene, 1, 2-phenylene, 4, and 4'-biphenylene, 1, 4-naphthalene-diyl, 2, 6-naphthalene-diyl, 9, and 10-anthracene-diyl are more specifically illustrated. Moreover, what was permuted by frames, such as a thiophene, a pyridine, and a quinoline, two places as an aromaticity heterocyclic compound radical containing a with a carbon numbers of four or more hetero atom is illustrated, and 2, 5-thienylene, 2, 3-pyridine-diyl, 2, 4-pyridine-diyl, 2, 5-pyridine-diyl, 2, 3-quinoline-diyl, 2, and 6-quinoline-diyl etc. is more specifically illustrated. From the ease of composition in the above radical, and a viewpoint that a high-melting compound is given 1, 4-phenylene, 4, and 4'-biphenylene, 2, 6-naphthalene-diyl, 9, 10-anthracene-diyl, 2, 5-thienylene, 2, 5-pyridine-diyl, 2, and 6-quinoline-diyl desirable still more preferably It is 1, 4-phenylene, 4, and 4'-biphenylene, 2, 6-naphthalene-diyl, 9, 10-anthracene-diyl, 2, and 5-pyridine-diyl.

[0015] Furthermore, Ar4 in the aromatic amine compound shown by the general formula (2) and (3) and Ar5 If it carries out, it is an aromaticity heterocyclic compound radical containing a with a carbon numbers of six or more aromatic hydrocarbon radical or a with a carbon numbers of five or more hetero atom. As a with a carbon numbers of six or more aromatic hydrocarbon radical, 1, 2, 4-benzene-Trier, 1, 3, 5-benzene-Trier, 1 and 2, 4-naphthalene-Trier, 1, 3, 5-naphthalene-Trier, 2 and 3, 6-naphthalene-Trier, 3, 5, 4'-biphenyl-Trier, 1, 2 and 4, 5-benzene-tetrayl, 2, 3, 6, 7-naphthalene-tetrayl, 3 and 4, 3', and 4'-biphenyl-tetrayl are mentioned, and 2, 4, 6-pyridine-Trier, 2 and 4, and 6-pyrimidine-Trier are illustrated as a with a carbon numbers of five or more aromaticity heterocyclic compound radical. They are 1, 3, 5-benzene-Trier, 1 and 3, 5-naphthalene-Trier, 2 and 3, 6-naphthalene-Trier, 3 and 5, 4'-biphenyl-Trier, 2 and 4, 6-pyridine-Trier, 2, 3 and 6, and 7-naphthalene-tetrayl among these more preferably.

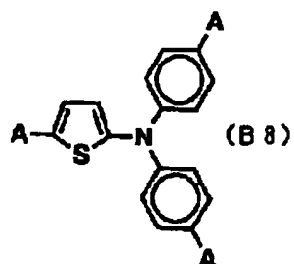
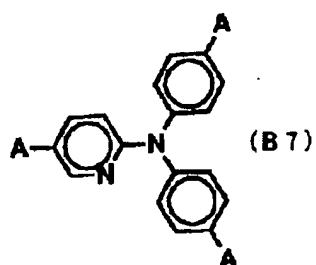
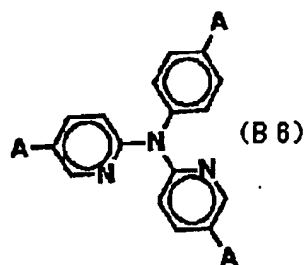
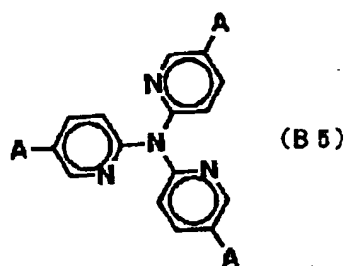
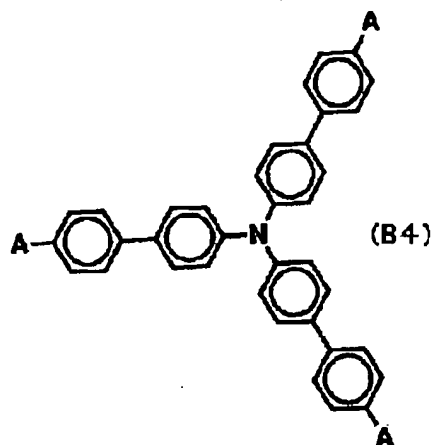
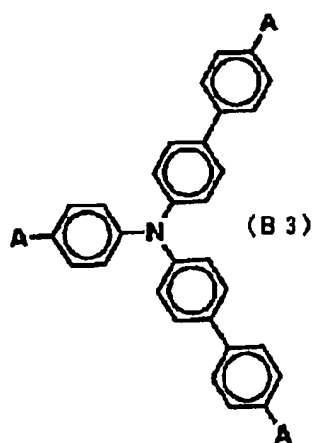
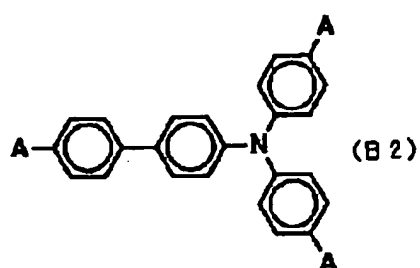
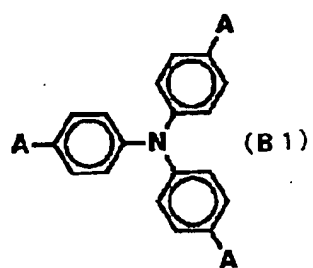
[0016] The diphenylamino radical expressed with general formula (4) - (12) that A1 -A10 described above in the aromatic amine compound shown by the general formula (1), (2), and (3) here, N-carbazolyl radical, a G 2-pyridylamino radical, an N-alkyl-N-phenylamino radical, The N-[3 and 4-pyrimide b] indolyl radical, an N-alkyl-N-2-pyridylamino radical, The N-[4 and 5-pyrimide b] indolyl radical, the N-[2 and 3-pyrimide b] indolyl radical, To the benzene ring of N-phenothiazinyl groups and those radicals, and a pyridine ring, the alkyl and the alkoxy group of carbon numbers 1-12, The radical chosen from the aryl and the aryloxy group, nitro group, and aromaticity heterocyclic compound radical of carbon numbers 6-14 is the derivative by which one or more piece nuclear substitution was carried out. Moreover, R8 and R12 are hydrogen and the alkyl group of carbon numbers 1-12 independently, respectively. A diphenylamino radical with good membrane formation nature, N-carbazolyl radicals, and those derivatives are desirable in these.

[0017] Here, as an alkyl group of carbon numbers 1-12, for example, it is a methyl group, an ethyl group, butyl, an octyl radical, etc., and a methyl group and an ethyl group are desirable. Or as an alkoxy group of carbon numbers 1-12, it is a methoxy group, an ethoxy radical, a propoxy group, a butoxy radical, a pentyloxy radical, a hexyloxy radical, a heptyloxy radical, etc., and a methoxy group and an ethoxy radical are desirable. As an aryl group, a phenyl group, 4-methylphenyl radical, 4-ethyl phenyl



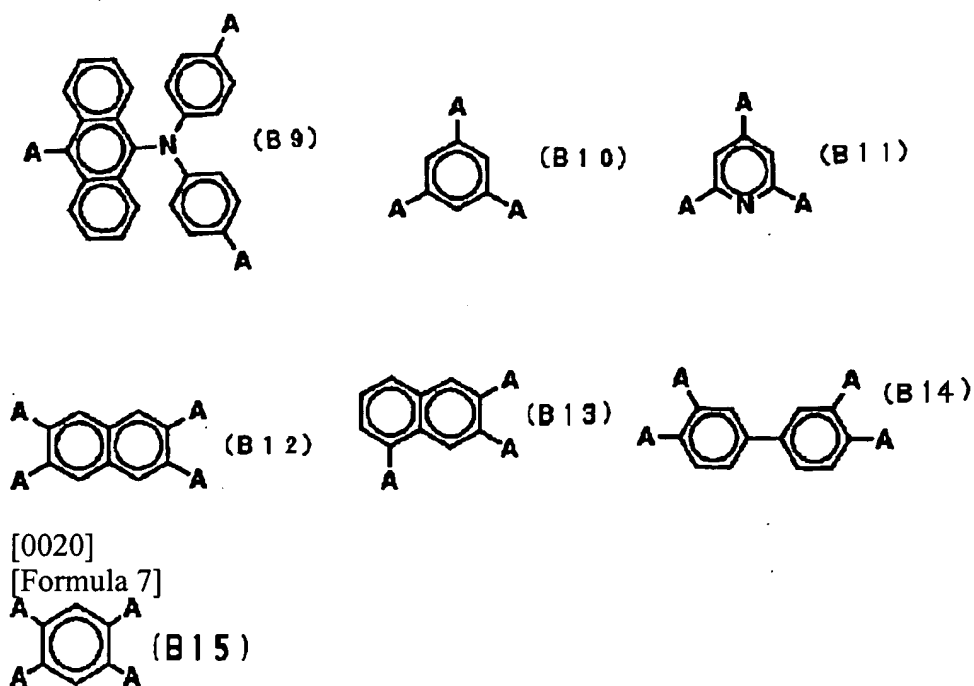
group, 4-propyl phenyl group, 4-buthylphenyl radical, 4-pentyl phenyl group, As 4-hexyl phenyl group, a 1-naphthalene radical, 2-naphthalene radical, and an aryloxy group, 4-methoxypheny radical, A 4-ethoxy phenyl group, a 4-propoxy phenyl group, a 4-butoxy phenyl group, A 4-pentyloxy phenyl group, a 4-hexyloxy phenyl group, a phenoxy group, 4-methylphenoxy radical, 4-ethyl phenoxy group, 4-propyl phenoxy group, 4-butyl phenoxy group, 4-pentyl phenoxy group, 4-hexyl phenoxy group, 4-methoxy phenoxy group, a 4-ethoxy phenoxy group, a 4-propoxy phenoxy group, a 4-butoxy phenoxy group, a 4-pentyloxy phenoxy group, and a 4-hexyloxy phenoxy group are illustrated. As a heterocyclic compound radical, 2-thienyl group, 2-pyridyl radical, 3-pyridyl radical, and 4-pyridyl radical are illustrated. Moreover, the alkyl group used in the N-alkyl-N-phenylamino radical of a general formula (7) and a general formula (9) and an N-alkyl-N-2-pyridylamino radical is an alkyl group of carbon numbers 1-12, and a methyl group and its ethyl group are desirable. The amine compound of a publication is listed to below as a concrete compound. It is the compound expressed with formula B1 - B15 of the following, and is [0018].

[Formula 5]



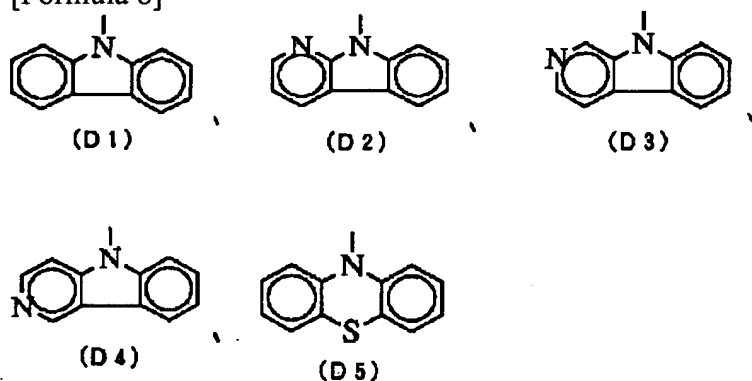
[0019]

[Formula 6]



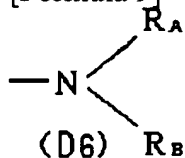
It comes out and A is [0021].

[Formula 8]



Or [0022]

[Formula 9]



It comes out and an expressing thing is mentioned. In addition, what A is expressed with D6 to is RA. And RB The thing of the combination shown in the 1st table of the following is illustrated concretely.

[0023]

[Table 1]

\*\* 1 Table ----- RA - RB ----- Phenyl Phenyl 2-methylphenyl 2-methylphenyl 3-methylphenyl 3-methylphenyl 4-methylphenyl 4-methylphenyl 2-ethylphenyl 2-ethylphenyl 3-ethylphenyl 3-ethylphenyl 4-ethylphenyl 4-ethylphenyl 4-tert-buthylphenyl 4-tert-buthylphenyl 4-methoxyphenyl 4-methoxyphenyl 4-ethoxyphenyl 4-ethoxyphenyl 2-nitrophenyl 2-nitrophenyl 4-(phenyl)phenyl 4-(phenyl)phenyl 4-(2-thienyl)phenyl 4-(2-thienyl)phenyl 4-(4'-methylphenyl)phenyl 4-(4'-methylphenyl)phenyl 2-thienyl 2-thienyl Phenyl Methyl Phenyl Ethyl

Phenyl 2-methylphenyl Phenyl 3-methylphenyl Phenyl 4-methylphenyl Phenyl 2-ethyl phenyl Phenyl 3-ethyl phenyl Phenyl 4-ethyl phenyl Phenyl 4-tert-buthylphenyl [0024]

[Table 2]

(Continuation)

----- Phenyl 4-methoxyphenyl Phenyl 4-ethoxy phenyl Phenyl 2-nitrophenyl  
Phenyl 2-pyridyl Phenyl 4-(phenyl) phenyl phenyl 4-(2-thienyl) phenyl phenyl 4-(4'-methylphenyl)  
phenyl phenyl 2-thienyl Methyl